CHEMISTRY, ADHESIVE AND COMPOSITE PROPERTIES OF LOW MOLECULAR WEIGHT PHENYLETHYNYL TERMINATED OLIGOMERS

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INTRODUCTION

As part of an on-going effort to develop high performance/high temperature structural resins, the chemistry, adhesive and composite properties of relatively low molecular weight phenylethynyl terminated oligomers are under investigation. PETI-5 is a phenylethynyl terminated oligomer that was developed at the NASA Langley Research Center and has undergone extensive evaluation as an adhesive and composite matrix resin[1-4]. This material is prepared at a calculated number average molecular weight (Mn) of 5000 g/mole from 3,3',4,4'-tetracarboxylic biphenyl dianhydride (BPDA), 85 mole percent 3,4'-oxydianiline (3,4'-ODA), 15 mole percent 1,3-bis(3-aminophenoxy)benzene (APB) and endcapped with 4-phenylethynylphthalic anhydride (PEPA) in N-methyl-2-pyrrolidinone (NMP). PETI-5 has displayed excellent processability and outstanding mechanical properties in both adhesive and composite forms. However, in the processing of complex structural parts, improvements in resin flow are desirable. In an attempt to improve the processability of PETI-5 (5000 g/mole) while maintaining equivalent properties, lower molecular weight versions (2500 and 1250 g/mole) were evaluated as adhesives and composite matrix resins.

The effect of lowering the molecular weight of PETI-5 on adhesive properties has been reported[5]. The material was prepared at Mns of 10,000, 5000 and 2500 g/mole. The PETI-5 5000 g/mole exhibited good processability and excellent tensile shear strengths[5].

Molecular weight distributions were determined on amide acid solutions in NMP by Gel Permeation Chromatography (GPC). Thin films, adhesive film and unsized IM-7 carbon fiber prepreg were prepared from amide acid solution. Imide powders were used for characterization by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and melt rheological analysis. The results of this preliminary evaluation of the PETI-5 1250 and 2500 g/mole are compared with those of PETI-5 (5000 g/mole).

EXPERIMENTAL

Oligomer Synthesis

The two different molecular weight versions of PETI-5 were prepared using the same procedure as that for the preparation of PETI-5 (5000 g/mole) [1].

Characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% (w/v) solutions of the amide acids in NMP at 25°C. DSC was conducted on a Shimadzu DSC-50 thermal analyzer at a heating rate of 20°C/min with the glass transition temperature (Tg) taken at the inflection point of the ΔT versus temperature curve. TGA was performed on a Seiko 200/220 instrument on cured polymer powder samples at a heating rate of 2.5°C/min in air at a flow rate of 15 cm^3/min. Brookfield viscosity was obtained on a Brookfield LVT Synchro-Lectric viscometer at 25°C. Rheological measurements were conducted on a Rheometrics System 4 rheometer. Sample specimen disks, 2.54 cm in diameter and 1.5 mm thick, were prepared by press molding imide powder at room temperature. The compacted resin disk was subsequently loaded in the rheometer fixture with 2.54 cm diameter parallel plates. The top plate was oscillated at a fixed strain of 5% and a fixed angular frequency of 10 rad/sec while the lower plate was attached to a transducer which recorded the resultant torque. Storage (G') and loss (G") moduli as a function of time (t) were measured at several temperatures. GPC was performed on a Waters 150C system equipped with a model 150R differential viscosity detector and a differential refractive index detector. GPC analyses were performed on dilute solutions of the amide acids in freshly distilled NMP containing 0.02M phosphorus pentoxide. The analyses were performed using a two column bank consisting of a linear Waters Styragel HT 6E column covering the molecular weight range of 10^3 to 10^7 g/mole in series with a Styragel HT 3 column covering the molecular weight range of 10^2 to 10^4 g/mole. A universal calibration curve was generated with Polymer Laboratories narrow molecular weight distribution polystyrene standards having molecular weights ranging from 500 to 2.75 x 10^6 g/mole.

Films

NMP solutions [~30%(w/w) solids] of the PETI-5 amide acid (PETAA) oligomers were centrifuged, the decantate doctored onto clean, dry plate glass and dried to a tack-free form in a low humidity chamber. The films on glass were dried in flowing air at 100, 225, and 350°C for 1 h each. Unoriented thin film tensile properties were determined according to ASTM D882 using four specimens per test condition.

Moldings

Powdered imide oligomers (approximately 8.5 g) were compression molded in a 3.2 cm^2 stainless steel mold by heating to 371°C under 0.30 MPa and holding for 1 h. Miniature compact tension specimens (1.6 cm X 1.6 cm X 0.95 cm thick) were machined from the moldings and subsequently tested to determine their fracture toughness (K_{Ic}, critical stress intensity factor) according to ASTM E399 using four specimens per test condition. Fracture energy (G_{Ic}, critical strain energy release rate) was calculated using the mathematical relationship, $G_{Ic} = (K_{Ic})^2/E$, where E is the tensile modulus of the material.

Adhesive Specimens

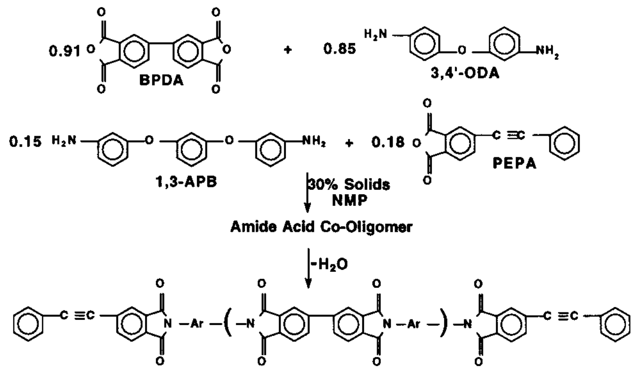
Adhesive tape was prepared by multiple coating of 112 E glass with an A-1100 finish with a 20% (w/w) NMP solution of the PETAA oligomers and subsequently stage-dried to 225°C in a forced air oven after each coat. After the appropriate thickness had been obtained, the tape was dried to 250°C to a final volatile content of ~2-4%. Titanium (Ti, 6Al-4V) tensile shear specimens with PASA-Jell 107 (Products Research and Chemical Corp., Semco Division) surface treatment were fabricated in a press at 350°C under various pressures for 1 h. Tensile shear strengths were determined according to ASTM D1002 using four specimens per test condition.

Composite Specimens

NMP solutions (35% solids w/w) of PETAA oligomers were used to coat unsized IM-7 carbon/graphite fiber (Hercules, Inc.) on a multi-purpose tape machine to afford unidirectional tape with resin contents ranging from 30-36% and volatile contents of 15-19%. The 1250 and 2500 g/mole solutions (35% solids) had Brookfield viscosities at room temperature of 2689 and 12,800 centipoise, respectively. Unidirectional laminates of different lay-ups and dimensions were fabricated in a vacuum press using stainless steel molds by heating to 371°C under 0.3-0.7 MPa and holding for 1 h. The composite panels were ultrasonically scanned, cut into specimens, and tested for various mechanical properties according to ASTM procedures.

RESULTS AND DISCUSSION

The synthesis of PETI-5 (5000 g/mole) is presented in Equation 1. The stoichiometric offsets used in the preparation of the PETI-5 2500 and 1250 g/mole were 0.83 and 0.68, respectively. Preliminary characterization determined on amide acid/NMP solutions and imide powders is presented in Table 1. The inherent viscosities and Tgs followed a trend based on molecular weight. In order to determine actual Mns, GPC was performed on the amide acids in NMP. The results presented in Table 2 are averages of duplicate runs of each sample. The Mns determined by GPC were higher than the calculated Mns.



Equation 1. Preparation of PETI-5 (5000 g/mole)

Table 1. Preliminary Characterization of PETI-5

Calculated Mn	η_{inh}, dL/g	Tg (Tm), °C Initial Cured	TGA, 5% Wt Loss, °C
1250	0.15	170(320) 288	489
2500	0.20	210(330) 277	497
5000	0.27	210(357) 270	503

Table 2. GPC Analysis of PETAA Oligomers

Calculated Mn	Mn, g/mole	Mw, g/mole	Mz, g/mole	Dispersity
1250	2050	3022	4307	1.47
2500	3308	6022	11670	1.82
5000	7914	13865	24260	1.75

The molecular weight distribution curve for the 1250 g/mole sample exhibited several well defined shoulder peaks at the low molecular weight end of the curve. The 2500 g/mole sample exhibited a more Gaussian distribution with only a slight shoulder at the low molecular weight end.

The effect of molecular weight on melt viscosity is presented in Table 3. As expected, the melt viscosity decreases with molecular weight. However, due to the thermal reaction of the phenylethynyl groups at temperatures near 300°C, these minimum melt viscosities are not stable.

Table 3. Melt Rheology of PETI-5

Calculated Mn	Minimum Melt Viscosity, Poise	Temp., °C
1250	50	335
2500	900	335
5000	10,000	371

It was of interest to determine the effect of molecular weight on neat resin fracture toughness. Moldings were prepared from the 2500 g/mole imide powder by compression molding under 0.3 MPa. The fracture toughness properties are presented in Table 4. Due to the excessive flow exhibited by the 1250 g/mole sample, quality moldings could not be fabricated.

Table 4. Neat Resin Fracture Toughness of PETI-5*

Calculated Mn	K_{Ic}, MPa·m$^{1/2}$	GIc, J/m^2
2500	3.9	4261
5000	3.9	4295
2500**	3.7	3878

*Moldings cured for 1 hr at 350°C
**Molding cured for 1 hr at 371°C

The PETI-5 (2500 g/mole) sample exhibited the same fracture toughness as that of the 5000 g/mole sample. This behavior is unexpected, typically a reduction in molecular weight between potential crosslinking sites causes a reduction in toughness. The effect of a higher temperature cure on the fracture toughness of the 2500 g/mole sample was relatively small.

Thin films were cast from amide acid/NMP solution and stage-dried and cured by heating through 1 hr at 350°C in a forced air oven. The tensile properties of the films are presented in Table 5. Due to excessive flow during the heating cycle, uniform films of acceptable quality for testing were not obtainable from the 1250 g/mole sample. However, the film was flexible and creasable indicating reasonable toughness.

Table 5. Thin Film Tensile Properties of PETI-5

Cal'cd Mn	Test Temp., °C	Ten. Str., MPa	Ten. Mod., GPa	Elong., %
2500	23 177	151.7 76.6	3.5 2.2	14 43
5000	23 177	129.6 84.1	3.1 2.3	32 83

Preliminary adhesive properties are presented in Table 6. All of the lap shear adhesive specimens exhibited cohesive failures. Adhesive film prepared from the 2500 g/mole PETI-5 also exhibited improved flatwise tensile strength compared to the 5000 g/mole.

Table 6. Preliminary Adhesive Properties of PETI-5

Calculated Mn (Bonding Cond.)	Test Temp., °C	Tensile Shear Str., MPa
2500 (0.1 MPa 350°C for 1 hr)	23 177 200	36.6 28.6 27.0
5000 (0.7 MPa 350°C for 1 hr)	23 177	49.0 29.7

The IM-7 carbon fiber laminate properties are presented in Table 7. The prepreg from the 1250 and 2500 g/mole PETI-5 exhibited acceptable tack at lower volatile content than the 5000 g/mole PETI-5. The 1250, 2500 and 5000 g/mole based laminates were fabricated under 0.3, 0.7 and 1.4 MPa, respectively and cured for 1 hour at 371°C. The laminates were processed in a vacuum press by heating to ~250°C for 1 hour under vacuum, pressure was subsequently applied and the laminates were heated to 371°C for 1 hour. The laminates were well consolidated and exhibited low void volumes. As expected, the PETI-5 (1250 g/mole) exhibited excessive flow and significant resin was lost during the laminate fabrication cycle even when processed under 0.3 MPa. The PETI-5 (1250 g/mole) exhibited better retention of open hole compression (OHC) properties at elevated temperatures, but a significant reduction in compression strength after impact (CAI). The PETI-5 2500 and 5000 g/mole exhibited identical CAI strength, modulus and microstrain. The CAI data further substantiates the identical neat resin fracture toughness exhibited by these two different molecular weight samples.

Table 7. IM-7/PETI-5 Laminate Properties*

Property	1250 g/mole	2500 g/mole	5000 g/mole
OHC Str., MPa RTD 177°C dry 177°C wet	 429.6 366.2 368.3	 458.6 395.2 344.1	 450.3 342.7 -------
CAI Str., MPa (25/50/25)	244.8	334.5	331.0
CAI Mod., GPa (25/50/25)	55.9	57.9	55.9
Microstrain, µin/in	4377	5908	5986

*Normalized to 62% fiber volume.

SUMMARY

PETI-5 (1250 and 2500 g/mole) were prepared and characterized. Neat resin, adhesive and composite properties were determined and compared with those of PETI-5 (5000 g/mole). Relative to PETI-5 (5000 g/mole), PETI-5 (2500 g/mole) exhibited improved processability and equivalency in the adhesive and composite properties measured thus far. This resin, in both adhesive film and prepreg form, has the potential to offer significant improvements in the processing of complex structural composite parts.

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